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**Anisotropy in magnetic and transport
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Abstract

We report the first measurements of anisotropy in magnetic susceptibility, magnetization, and electrical resistivity using single crystals of GdTSb_3 ($T=\text{Cr, V}$). GdTSb_3 is a quasi-two dimensional system with orthorhombic crystal structure (space group $Pbcm$). Unlike the other light rare earth chromium antimonides ($R = \text{Ce-Nd, Sm}$), in which two magnetic transitions are observed, GdCrSb_3 undergoes a single ferrimagnetic transition at $T_C=86$ K, which is evident in both the magnetic susceptibility and electrical resistivity. Within the b - c plane, GdCrSb_3 is found to have metallic behavior from 5 K to 300 K, but it is found to have insulating behavior ($d\rho_a/dT < 0$) along the stacking axis. GdVSb_3 is found to have a Néel transition at 5 K due to the localized Gd ions, but no ferromagnetic transition.

Key words: magnetism, antimonides, resistivity, $R\text{CrSb}_3$

PACS: 75.30.Gw, 72.80.Ga, 72.15.-v, 75.30.Cr

1 Introduction

The family of compounds, $RCrSb_3$ ($R = \text{La-Nd, Sm, Gd-Dy}$), have had many investigations in the literature due to their unique magnetic and electrical transport properties[1–12]. The parent member in the series, $LaCrSb_3$, has been studied in depth [3–5] because it has only one magnetic ion, Cr, yet it has a very complex magnetic phase diagram. It has been found to have a Curie temperature at $T_C=132$ K, followed by a spin reorientation phase for $T < 98$ K and $H < 250$ G due to the unconventional magnetism involving the coexistence of local and itinerant Cr moments.[4,5] While the itinerant ferromagnetic (FM) phase continues to exist for $RCrSb_3$ ($R = \text{Ce-Nd, Sm}$), a second low temperature magnetic phase occurs due to the ordering of the rare-earth ions.[6–10] $SmCrSb_3$ was found to be unique in the series due to the presence of a first order AFM transition at 30 K due to the ordering of the Sm ions.[10] Polycrystalline samples of $R=\text{Gd, Tb, and Dy}$ have been investigated,[7,12] which show only one AFM transition, but the value of the transition temperature is still debated. Single crystal electrical resistivity measurements have also been collected along the c -axis,[12] but to our knowledge, this is the first report of the magnetization and electrical resistivity along all three principle axis of $GdCrSb_3$ using high quality single crystals.

2 Experimental Technique

Single crystals of $GdTSb_3$ were prepared from ingots of the elements [Gd from Ames Laboratory; Cr (99.996%), V (99.5%), and Sb (99.99%) from Alfa Aesar], and the growth procedure has been previously described[4]. $GdTSb_3$

crystallizes in an orthorhombic structure (space group $Pbcm$), [1,2] and consists of two distinct planar layers of Cr and Sb perpendicular to the a -axis which are separated by Gd ions (see Fig. 1a). The first of these layers consists of chains of Cr atoms extending along the c direction, with Sb atoms forming face sharing (edge sharing) octahedra along the c -axis (b -axis). The Gd ions lie in a checker board type pattern which alternates above and below the Sb plane. This quasi-2D crystal structure suggests that anisotropy may play a crucial role in understanding its properties. The lattice parameters were determined using a commercial Scintag x-ray diffractometer using a Si standard, and a least squares fit to a minimum of 20 peaks. The lattice constants for $GdCrSb_3$ were determined to be $a = 12.75(6)$ Å, $b = 6.15(2)$ Å, and $c = 6.01(4)$ Å, and for $GdVSb_3$, $a = 12.82(2)$ Å, $b = 6.22(3)$ Å, and $c = 5.96(2)$ Å.

Magnetization and magnetic susceptibility measurements were taken with a commercial superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMSR2) in the temperature range 2-350 K and $-55 \text{ kG} \leq H \leq 55 \text{ kG}$. High field magnetization measurements were collected using a vibrating sample magnetometer in a field range of $0 \leq H \leq 31 \text{ T}$ at the National High Magnetic Field Laboratory. Electrical resistivity measurements were performed using a standard four probe technique in the temperature range 5-295 K. All measurements were collected on as grown samples.

3 Magnetization

One expects $GdCrSb_3$ to have somewhat different properties than the light rare-earth antimonides in the series because Gd^{3+} has a half full f -electron shell, and therefore has zero orbital angular momentum and a large effective

moment ($\mu_{eff} = 7.94 \mu_B$ according to Hund's Rules). Fig. 1 shows the field-cooled magnetization as a function of temperature with an applied field of 1 kG. Unlike the previous members in the series, there is no evidence of a FM phase for GdCrSb_3 , but it does undergo a magnetic transition at $T_C=86$ K. This is most easily observed as a peak along the c -axis, and is consistent with this being the easy axis of a ferrimagnetic phase, and is the only apparent magnetic phase transition. Fig. 1 also shows an upturn in the susceptibility at low temperatures along both the a and b -axis, which may be due to the Cr vacancies which are known to exist in these compounds.[5] These vacancies may play a role in the discrepancies in the reported transition temperatures. For example, Deakin *et al.* report a value of 92 K for the magnetic transition,[12] and Leonard *et al.* report a value of 26 K.[7]

The high temperature inverse susceptibility ($T > 200$ K) was fit to a modified Curie–Weiss law, $1/(\chi - \chi_0) = (T - \theta)/C$, where χ_0 is the temperature independent susceptibility, θ is the Curie temperature, and C is the Curie constant. The data is shown in Fig. 1b, with the values from the fit given in Table 1. The expected value of χ_0 can be approximated to be approximately -1×10^{-4} emu/mol[13], which is an order of magnitude larger than what is found for this system. This, as well as the metallic electrical resistivity, is consistent with itinerant behavior for the RCrSb_3 family. Table 1 also lists the effective moment of GdCrSb_3 for each axis. A polycrystalline average gives $\mu_{eff} = 9.21 \mu_B/\text{f.u.}$, which is larger than the value predicted by Hund's Rules, but close to the value of $8.16 \mu_B/\text{f.u.}$, obtained by Deakin *et al.*[12] They suggest that this large value is an indication of the strong interactions of the $3d$ and $4f$ moments above the ordering temperature. The downward curvature seen in the inverse susceptibility near T_C (Fig. 1b) is the expected behavior

for a ferrimagnetic system.

The magnetization as a function of applied magnetic field (Fig. 2) also suggests that below $T_C=86$ K, GdCrSb_3 is ferrimagnetic. At 5 K, one finds that M_a and M_b linearly increase with increasing field, while M_c undergoes a spin-flop transition at 26 kG, which implies that the easy axis is parallel to the Cr chains (the c -axis). The inset to Fig. 2 shows the magnetization along the a -axis up to 31 T at 10 K and 75 K. The a -axis magnetization begins to saturate just below 15 T to a value of $5.6 \mu_B/\text{f.u.}$, which is smaller than the predicted saturation value of Gd^{3+} ($\sigma = gJ = 7 \mu_B$).

4 Electrical Resistivity

The distinctive behavior of the magnetization leads one to expect unique electrical resistivity as well, and Fig. 3 shows that this is found to be true. The initial high temperature behavior of the electrical resistivity is similar to both LaCrSb_3 and SmCrSb_3 , [4,10] with positive temperature dependence for the in-plane (b - c plane) resistivity, and non-metallic ($d\rho/dT < 0$) temperature dependence for the out of plane (a -axis) resistivity. Below T_C , the in-plane resistivity continues to have a positive slope. While the residual resistivity ratio for both axis ($RRR_b = 0.45$, $RRR_c = 0.70$) is small, the values are larger than what has been observed in other members of the series. For example it is approximately three times larger than LaCrSb_3 ($RRR_b = 0.16$, $RRR_c = 0.23$), [4] and twice as large as SmCrSb_3 ($RRR_b = 0.19$, $RRR_c = 0.34$). [10] This small value is likely due to the large number of Cr vacancies, such as has been observed for LaCrSb_3 . [5] For $R=\text{La-Nd}$, and Sm, the resistivity along the a -axis (the stacking axis) was found to have a change in the sign of the slope below

T_C , but for GdCrSb_3 , a kink is observed, below which the resistivity continues to rise with an increased slope. Fig. 3a shows that a Fisher-Langer-type anomaly is present along the b -axis (as well as the c -axis, data not shown), only the peak has become broadened compared with LaCrSb_3 and SmCrSb_3 . Below T_C , Fig. 3b shows that the in-plane resistivity decreases as $T^{3/2}$, which is the same behavior found for both $R=\text{La}$ [4] and Sm . [10] This temperature dependence for the electrical resistivity is common for a FM systems in which the scattering length is reduced from an ideal system, [14] which suggests that the in-plane scattering mechanism for GdCrSb_3 is similar to that found for $R=\text{La}$ and Sm .

5 GdVSb_3

LaVSb_3 was found to be a non-magnetic counterpart to LaCrSb_3 . Therefore, in order to understand the properties of GdCrSb_3 in the absence of itinerant magnetism, isostructural GdVSb_3 was investigated. The in-plane anisotropy in the magnetization for GdVSb_3 was found to be zero. Therefore Fig. 4a shows only the data along the c -axis, with a modified Curie–Weiss fit between 45 K and 330 K, and the resulting parameters given in Table 1. The low temperature susceptibility is shown in the inset to Fig. 4a in which a peak is found at $T_N=5$ K. This is very similar behavior to that seen in SmVSb_3 . [10] The values obtained are close to the expected value for Gd^{3+} of $\mu_{eff} = 7.94 \mu_B$.

The electrical resistivity normalized at room temperature is shown in Fig. 4b. Both axes have similar behavior to what was found for SmVSb_3 , [10] only the AFM ordering temperature for GdVSb_3 is large enough that an initial increase in the resistivity just above 5 K can be seen. Due to the small thickness, it

was not possible to measure the electrical resistivity along the a -axis.

6 Discussion

GdVSb₃ is isostructural to GdCrSb₃, but, like LaVSb₃, in which the magnetic susceptibility is small and temperature independent due to the absence of itinerant magnetism,[4] the magnetic susceptibility of GdVSb₃ is due only to the localized $4f$ -electrons of Gd³⁺. It is magnetically isotropic, unlike GdCrSb₃, and it has a Néel temperature near 5 K due to ordering of the $4f$ -moments. This points to the importance of the interactions between the itinerant $3d$ -electrons and the localized $4f$ -electrons in determining the properties of the $RCrSb_3$ family of materials.

$RCrSb_3$ ($R = \text{Ce-Nd, and Sm}$) are all found to undergo two magnetic transitions due to the itinerant FM phase of the $3d$ -electrons at high temperatures, followed by a low temperature ordering of the localized rare-earth ions.[6–10] For $R = \text{Sm and Gd}$, the interactions between the itinerant $3d$ and localized $4f$ -electrons are strong enough to bring about unique properties in these two materials. SmCrSb₃ was found to undergo a first order Néel transition at 30 K, and isothermal magnetization hysteresis loops observed at low fields below T_N suggest that the itinerant $3d$ -electrons continue to exhibit FM interactions, but the localized $4f$ -moments nearly cancel out the macroscopic magnetization of the sample.[10] Although our magnetization results can not probe the microscopic behavior of the $3d$ and $4f$ -moments, it would be consistent with the SmCrSb₃ results for the compound to be described by two independent, yet heavily interacting subsystems: one composed of itinerant $3d$ -electrons, and a second of anti-aligned localized $4f$ -moments.

It is believed that similar behavior is found for GdCrSb_3 , but for this material, both magnetic lattices order at the same temperature and appear to be antiparallel, resulting in a complex ferrimagnetic ordering. The downward curvature in $1/\chi$ just above T_C (Fig. 1b) is indicative of ferrimagnetism. Recent ac magnetic susceptibility measurements of GdCrSb_3 [12] show a significant imaginary component to the magnetic susceptibility, which provides further support for a ferrimagnetic phase. The spin-flop transition at 26 kG and 5 K is also consistent with a ferrimagnetic phase, and indicates the easy axis is along the c -axis. At 30 K, Deakin *et al.*[12] observed a maximum in the magnetoresistance at 30 kG when the magnetic field was oriented along the c -axis, and no maximum with the magnetic field aligned perpendicular to the c -axis. The in-plane $T^{3/2}$ resistivity behavior of GdCrSb_3 is also similar to both LaCrSb_3 and SmCrSb_3 , suggesting that the scattering mechanisms are similar, which would again be consistent with itinerant ferromagnetism due to the $3d$ -electrons below $T_C=86$ K, but strong interactions with the $4f$ -moments resulting in an overall ferrimagnetic phase.

The transition temperatures for $R\text{CrSb}_3$ ($R = \text{La-Nd, Sm, and Gd}$) are plotted vs the de Gennes factor, $DG = (g-1)^2 J(J+1)$, in Fig. 5. This shows that the FM transition due to the itinerant $3d$ -electrons of the Cr ions, as well as the localized $4f$ -moments of the rare-earth ions scale with the de Gennes factor. In addition, both transition temperatures converge at the ferrimagnetic transition found for GdCrSb_3 . The result provides further evidence of the behavior of the ferrimagnetic phase in which the Gd and Cr moments strongly interact, and become anti-aligned at the same temperature. The inset to Fig. 5 shows the paramagnetic Curie temperature, averaged over the three principle axis, for each member in the series. Although a general downward trend is observed, it

is not clear if there is a strong correlation between the de Gennes factor and the paramagnetic Curie temperature, and a doping study on the rare-earth site is underway in order to clarify this relationship. However, the general trend shows that both the rare-earth magnetic ordering temperature and the paramagnetic Curie temperature scale with the de Gennes factor.

7 Conclusions

While above $T_C=86$ K, GdCrSb_3 has very similar magnetic and electrical resistivity properties to those of the light rare-earth chromium antimonides, at lower temperatures very different behavior is found. Both the magnetic susceptibility vs temperature and the magnetization vs field indicate that the system enters a ferrimagnetic phase below 86 K. It is within this ferrimagnetic phase that the anisotropy of the electrical resistivity is clearly evident with insulating behavior found along the stacking axis (the a -axis), and metallic behavior found within the b - c plane. In addition, the de Gennes scaling of itinerant FM and localized rare-earth ordering transition temperatures for RCrSb_3 converge to the 86 K transition of GdCrSb_3 . These are all indications of a ferrimagnetic phase in which the itinerant $3d$ and localized $4f$ moments are heavily interacting, and anti-aligned.

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Fig. 1. Field cooled magnetization for the three principle axis of GdCrSb_3 . The insets show (a) the $RT\text{Sb}_3$ crystal structure, and (b) the high temperature fit to a Curie–Weiss law.

Fig. 2. Magnetization as a function of field for GdCrSb_3 at 5 K. The inset shows the magnetization along the a -axis at 10 K up to 31 T.

Fig. 3. Electrical resistivity of GdCrSb_3 normalized to room temperature. The insets show (a) $d\rho_b/dT$ with a broad peak at the ferrimagnetic Curie temperature, and (b) the $T^{3/2}$ behavior of the resistivity below 86 K.

Fig. 4. a) Inverse magnetic susceptibility along the c -axis for GdVSb_3 with an applied field of 10 kG, with the low temperature susceptibility displayed in the inset showing the AFM transition at 5 K. b) The in-plane electrical resistivity of GdVSb_3 normalized to room temperature.

Fig. 5. The de Gennes scaling for $R\text{CrSb}_3$ which show both the Curie temperature due to the Cr ions, and the low temperature ordering due to the rare-earth ions. Both transition temperatures converge at the 86 K transition for $R = \text{Gd}$. Inset shows the paramagnetic Curie temperature, averaged over the three principle axis, which also scales with the de Gennes factor (data from [4,10,16]).

Table 1

Hight temperature Curie-Weiss parameters for $\text{Gd}T\text{Sb}_3$ ($T=\text{Cr, V}$). The error in χ_0 is 10%. Sample dimensions of GdVSb_3 precluded the measurement along the a -axis.

GdCrSb_3			
axis	χ_0 (10^{-3} emu/mol)	μ_{eff} ($\mu_B/\text{f.u.}$)	θ (K)
a	-1.27	7.89 ± 0.13	-90 ± 12
b	-4.60	10.3 ± 0.3	-88 ± 11
c	-2.45	9.45 ± 0.25	-86 ± 13
GdVSb_3			
b	-0.57	$8.25 \pm .01$	21.5 ± 0.1
c	-.085	$8.33 \pm .01$	-22.9 ± 0.1









